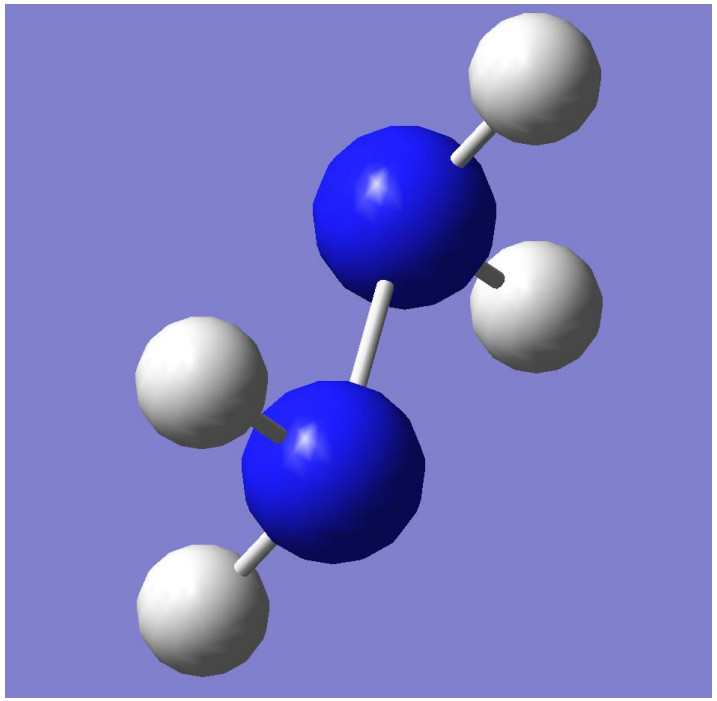
ADAM MICKIEWICZ UNIVERSITY IN POZNAŃ

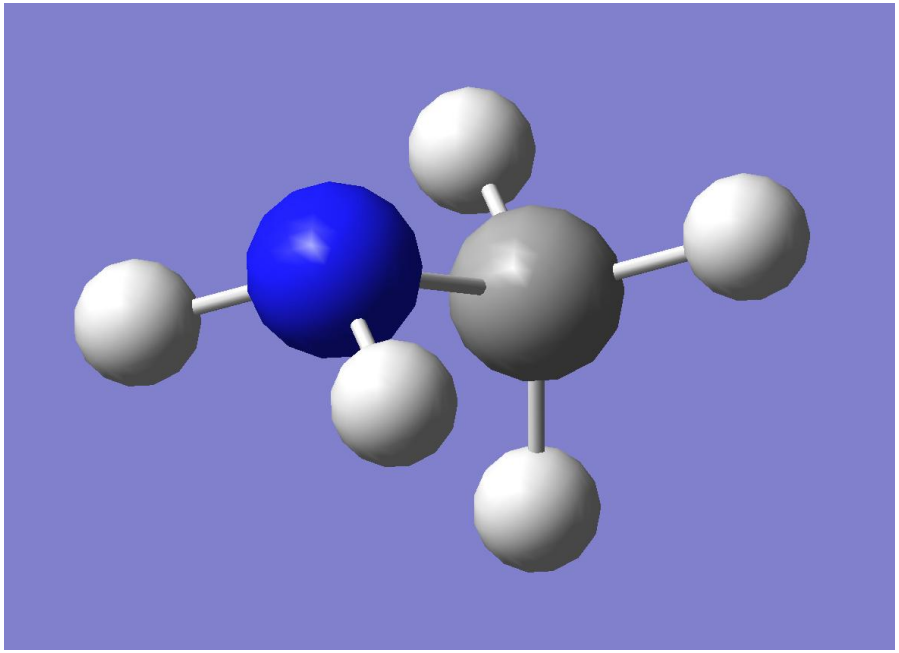
FLOPPY MOLECULES WITH INTERNAL ROTATION AND INVERSION

Marek Kręglewski

Hydrazine and methylamine



N_2H_4



CH_3NH_2

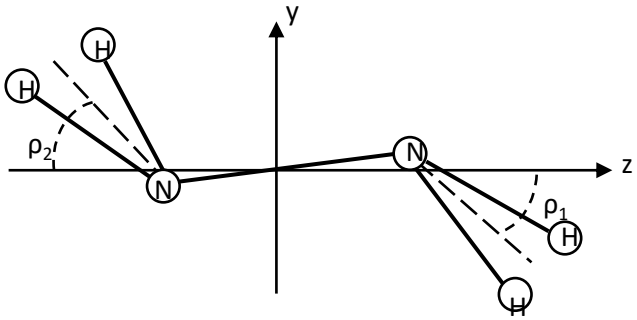
Rovibrational Hamiltonian of a floppy molecule[a]

Explicit rovibrational Hamiltonian	Effective Hamiltonian
Permutation- inversion group of a molecule	
Definition of small and large amplitude coordinates	
Differences between linear and curvilinear coordinates	
Transformations of coordinates in the PI group	Transformations of configurations in the PI group
Hamiltonian in vibrational and rotational coordinates	Effective group-theoretical Hamiltonian
Symmetrized rovibrational basis functions	Symmetrized linear combinations of configurations
Calculation of the Hamiltonian matrix elements	
Labels (assignment of quantum numbers) on eigenvalues	
Results: geometry and potential function	Results: rovibrational and tunneling parameters

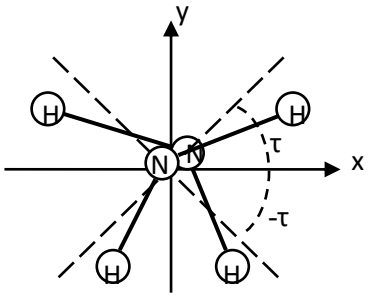
[a] For rotational problem see: J.T.Hougen, „Strategies for advanced applications of permutation-inversion groups to their microwave spectra of molecules with large amplitude motions", J.Mol.Spectrosc. **256** (2009) 170-185

PI group $G_{16}^{(2)}$ for hydrazine

Transformation from laboratory to molecular coordinates:



inversion as a motion around a local mass center of the NH_2 group



rotation and counter-rotation

$$\boldsymbol{R}_i = \boldsymbol{R} + \boldsymbol{S}^{-1}(\chi,\theta,\varphi)\cdot\left[\boldsymbol{a}_i(\tau,\rho_1,\rho_2) + \boldsymbol{d}_i\right] \quad i = 1,\ldots,6$$

PI group symmetry generators of the $G_{16}^{(2)}$ group:

a=(34)(1526)*

b=(34)(15)(26)

c=E*

d=double group

Transformations of rotational and LAV coordinates				
E	***a***	***b***	***c***	***d***
χ	$\chi+\pi/2$	$-\chi$	$-\chi$	$\chi+\pi$
θ	θ	$\pi-\theta$	$\pi-\theta$	θ
φ	φ	$\varphi+\pi$	$\varphi+\pi$	φ
τ	$-\tau+\pi/2$	τ	$-\tau+\pi$	$\tau+\pi$
ρ_1	ρ_2	$-\rho_2$	$-\rho_1$	ρ_1
ρ_2	$-\rho_1$	$-\rho_1$	$-\rho_2$	ρ_2

Character table of $G_{16}^{(2)}$

	e	d	a^2	a^2 d	c cd	a^2c a^2cd	b a^2b	bd a^2bd	bc a^2bc	a^2bc bcd	a a^3 ad a^3d	ac a^3c acd a^3cd	ab a^3b abd a^3bd	abc a^3bc abcd a^3bcd	Nuclear spin weights
A_{1g}^{+}	1	1	1	1	1	1	1	1	1	1	1	1	1	1	6
A_{2u}^{+}	1	1	1	1	1	1	-1	-1	-1	-1	1	1	-1	-1	36
A_{1u}^{-}	1	1	1	1	-1	-1	1	1	-1	-1	1	-1	1	-1	45
A_{2g}^{-}	1	1	1	1	-1	-1	-1	-1	1	1	1	-1	-1	1	3
B_{1g}^{+}	1	1	1	1	1	1	1	1	1	1	-1	-1	-1	-1	45
B_{2u}^{+}	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1	3
B_{1u}^{-}	1	1	1	1	-1	-1	1	1	-1	-1	-1	1	-1	1	6
B_{2g}^{-}	1	1	1	1	-1	-1	-1	-1	1	1	-1	1	1	-1	36
E^{+}	2	2	-2	-2	2	-2	0	0	0	0	0	0	0	0	27
E^{-}	2	2	-2	-2	-2	2	0	0	0	0	0	0	0	0	27
E_1	2	-2	2	-2	0	0	2	-2	0	0	0	0	0	0	-
E_2	2	-2	2	-2	0	0	-2	2	0	0	0	0	0	0	-
E_g	2	-2	-2	2	0	0	0	0	2	-2	0	0	0	0	-
E_u	2	-2	-2	2	0	0	0	0	-2	2	0	0	0	0	-

Rotation-inversion-torsion functions belong to one of 10 red species

Some rotation or inversion functions belong to these species

Rotation-torsion-inversion Hamiltonian for N_2H_4

$$H_{rit} = \frac{1}{2}\mu^{\frac{1}{4}} \sum_{\alpha\beta} J_\alpha \mu_{\alpha\beta} \mu^{-\frac{1}{2}} J_\beta \mu^{\frac{1}{4}} + V(\tau, \rho_1, \rho_2)$$

$$\alpha, \beta = x, y, z, \tau, \rho_1, \rho_2$$

J_x, J_y, J_z components of the angular momentum operator ***J***

$J_\eta = -i\hbar \, \partial / \partial \eta$, $\eta = \tau, \rho_1, \rho_2$ operators of the torsion and inversion momenta

Potential function expanded in Fourier series

$$V(\tau, \rho_1, \rho_2) = V_i(\rho_1) + V_i(\rho_2) + V_{ii}(\rho_1, \rho_2) + V_t(\tau) + V_{it}(\tau, \rho_1, \rho_2)$$

$V_i(\rho_k) = a_0 + a_1 \cos\rho_k + a_2 \cos 2\rho_k + a_3 \cos 3\rho_k + a_4 \cos 4\rho_k$ $\quad k = 1,2$ „single” inversion

$V_{ii}(\rho_1, \rho_2) = V_{22} \cos 2\rho_1 \cos 2\rho_2$ coupling of inversions

$V_t(\tau) = V_4 \cos 4\tau + V_8 \cos 8\tau$ „pure” torsion

$V_{it}(\tau, \rho_1, \rho_2) = V_{222} \sin 2\rho_1 \sin 2\rho_2 \cos 2\tau$ coupling inv-torsion

Inverse moment of inertia tensor

$$\boldsymbol{\mu} = \begin{bmatrix} I_{xx} & I_{xy} & I_{xz} & I_{x\tau} & I_{x\rho_1} & I_{x\rho_2} \\ I_{yx} & I_{yy} & I_{yz} & I_{y\tau} & I_{y\rho_1} & I_{y\rho_2} \\ I_{zx} & I_{zy} & I_{zz} & I_{z\tau} & I_{z\rho_1} & I_{z\rho_2} \\ I_{\tau x} & I_{\tau y} & I_{\tau z} & I_{\tau\tau} & I_{\tau\rho_1} & I_{\tau\rho_2} \\ I_{\rho_1 x} & I_{\rho_1 y} & I_{\rho_1 z} & I_{\rho_1\tau} & I_{\rho_1\rho_1} & I_{\rho_1\rho_2} \\ I_{\rho_2 x} & I_{\rho_2 y} & I_{\rho_2 z} & I_{\rho_2\tau} & I_{\rho_2\rho_1} & I_{\rho_2\rho_2} \end{bmatrix}^{-1}$$

rotation

torsion

inversion

Tensor inverse to the generalized moment of inertia tensor ***I***

Elements of $\boldsymbol{\mu}$ expanded in Fourier series in τ, ρ_1, ρ_2 , examples below:

Elements of A_{1g}^{+} symmetry:

$$\left(\mu_{\rho_1\rho_1} + \mu_{\rho_2\rho_2}\right) = \sum b_1(k,k',l_1)\left(\cos k\rho_1 \cos k'\rho_2 + \cos k'\rho_1 \cos k\rho_2\right)\cos l_1\tau + \sum b_2(k,k',l_2)\left(\sin k\rho_1 \sin k'\rho_2 + \sin k'\rho_1 \sin k\rho_2\right)\cos l_2\tau$$

$$k,k' = 0,1,2,\ldots \qquad l_1 = 0,4,\ldots \qquad l_2 = 2,6,\ldots$$

Elements of E_g symmetry:

$$\begin{pmatrix} \mu_{xz} \\ \mu_{yz} \end{pmatrix} = \sum b(k,k',l)\left(\sin k\rho_1 \cos k'\rho_2 \pm \cos k'\rho_1 \sin k\rho_2\right)\begin{pmatrix} \sin l\tau \\ \cos l\tau \end{pmatrix}$$

$$k = 1,2,\ldots \qquad k' = 0,1,2,\ldots \qquad l = 1,3,\ldots$$

Basis functions

	function	from equation
Rotational	$\Psi_r = \left\| J, K \right\rangle$	$H_r = \frac{1}{4}\left(\mu_{xx} + \mu_{yy}\right)\left(J^2 - J_z^2\right) + \frac{1}{2}\mu_{zz} J_z^2$
Torsional	$\Psi_t \equiv \left\| m \right\rangle = \sum_m c_m \left[N_m \left(e^{im\tau} \pm e^{-im\tau} \right) \right]$	$H_t = \frac{1}{2}\mu_{\tau\tau} J_\tau^2 + V_t(\tau)$
Inversion	$\Psi_{i1} \equiv \left\| v_1 \right\rangle = \sum_n c_n \left[N_n \left(e^{in\rho_1} \pm e^{-in\rho_1} \right) \right]$	$H_i = \frac{1}{2}\mu_{\rho_1\rho_1} J_{\rho_1}^2 + V_i(\rho_1)$
	$\Psi_{i2} \equiv \left\| v_2 \right\rangle = \sum_n c_n \left[N_n \left(e^{in\rho_2} \pm e^{-in\rho_2} \right) \right]$	

$$\Psi_{rti} = \Psi_r \Psi_t \Psi_{i1} \Psi_{i2} = \left| J, k \right\rangle \left| m \right\rangle \left| v_1 \right\rangle \left| v_2 \right\rangle$$

J, k, m, v_1, v_2 - quantum numbers

Symmetrized rotational, torsional and inversion functions

Function	notation	expression	symmetry species
rotational	$\left\|J,K^{\pm}\right\rangle$	$N_K\left(\left\|J,K\right\rangle \pm (-1)^J \left\|J,-K\right\rangle\right)$	$A_{1g}^{+}, A_{2g}^{-}, B_{1g}^{+}, B_{2g}^{-}, E_g$
torsional	$\left\|m^{\pm}\right\rangle$	$N_m\left(\left\|m\right\rangle \pm \left\|-m\right\rangle\right)$	$A_{1g}^{+}, A_{1u}^{-}, B_{1g}^{+}, B_{1u}^{-}, E_1$
inversion	$\left\|v_1,v_2^{\pm}\right\rangle$	$N_\upsilon\left(\left\|\upsilon_1(1),\upsilon_2(2)\right\rangle \pm \left\|\upsilon_2(1),\upsilon_1(2)\right\rangle\right)$	$A_{1g}^{+}, A_{2u}^{+}, B_{1g}^{+}, B_{2u}^{+}, E^{-}$

Symmetrized basis functions

$$\psi_{rit}^{(1)} \equiv \left| J,K,m,\upsilon_1,\upsilon_2 \right\rangle^{(1)} =$$
$$= N_{rit}\left\{\left(1+(-1)^{K+m}+\zeta(-1)^{K+\upsilon_1+\upsilon_2}+\zeta(-1)^{m+\upsilon_1+\upsilon_2}\right)\right\}$$
$$\left\{\left(\left|J,K\right\rangle+\left|J,-K\right\rangle\right)\left(\left|m\right\rangle+\beta(-1)^J\left|-m\right\rangle\right)\left(\left|\upsilon_1,\upsilon_2\right\rangle+\gamma(-1)^{J+K}\left|\upsilon_2,\upsilon_1\right\rangle\right)+\right.$$
$$\left.+\left(\alpha(-1)^{\upsilon_1} i^{K+m}\right)\left(\left|J,K\right\rangle-\left|J,-K\right\rangle\right)\left(\left|m\right\rangle-\beta(-1)^J\left|-m\right\rangle\right)\left(\left|\upsilon_1,\upsilon_2\right\rangle-\gamma(-1)^{J+K}\left|\upsilon_2,\upsilon_1\right\rangle\right)\right\}$$

$$\psi_{rit}^{(2)} \equiv \left| J,K,m,\upsilon_1,\upsilon_2 \right\rangle^{(2)} =$$
$$= N_{rit}\left\{\left(1+(-1)^{K+m}+\zeta(-1)^{K+\upsilon_1+\upsilon_2}+\zeta(-1)^{m+\upsilon_1+\upsilon_2}\right)\right\}$$
$$\left\{\left(\left|J,K\right\rangle+\left|J,-K\right\rangle\right)\left(\left|m\right\rangle+\beta(-1)^J\left|-m\right\rangle\right)\left(\left|\upsilon_1,\upsilon_2\right\rangle+\gamma(-1)^{J+K}\left|\upsilon_2,\upsilon_1\right\rangle\right)+\right.$$
$$\left.-\left(\alpha(-1)^{\upsilon_2} i^{K+m}\right)\left(\left|J,K\right\rangle-\left|J,-K\right\rangle\right)\left(\left|m\right\rangle-\beta(-1)^J\left|-m\right\rangle\right)\left(\left|\upsilon_1,\upsilon_2\right\rangle-\gamma(-1)^{J+K}\left|\upsilon_2,\upsilon_1\right\rangle\right)\right\}$$

the terms which differentiate two types of symmetrized functions

the terms which define the allowed parity of quantum numbers

Symmetry	α	β	γ	ζ
A_{1g}^{+}	+1	+1	+1	+1
A_{2u}^{+}	-1	+1	-1	+1
A_{1u}^{-}	-1	-1	+1	+1
A_{2g}^{-}	+1	-1	-1	+1
B_{1g}^{+}	-1	+1	+1	+1
B_{2u}^{+}	+1	+1	-1	+1
B_{1u}^{-}	+1	-1	+1	+1
B_{2g}^{-}	-1	-1	-1	+1
E^{+}	0	-1	0	-1
E^{-}	0	+1	0	-1

Selected matrix elements

The rotation-torsion-inversion Hamiltonian is expressed in terms of operators J_α (α=x,y,z,τ,ρ_1,ρ_2) and linear combination and products of cos and sin functions of τ, ρ_1 and ρ_2.
Thus a selected matrix element can assume the following form:

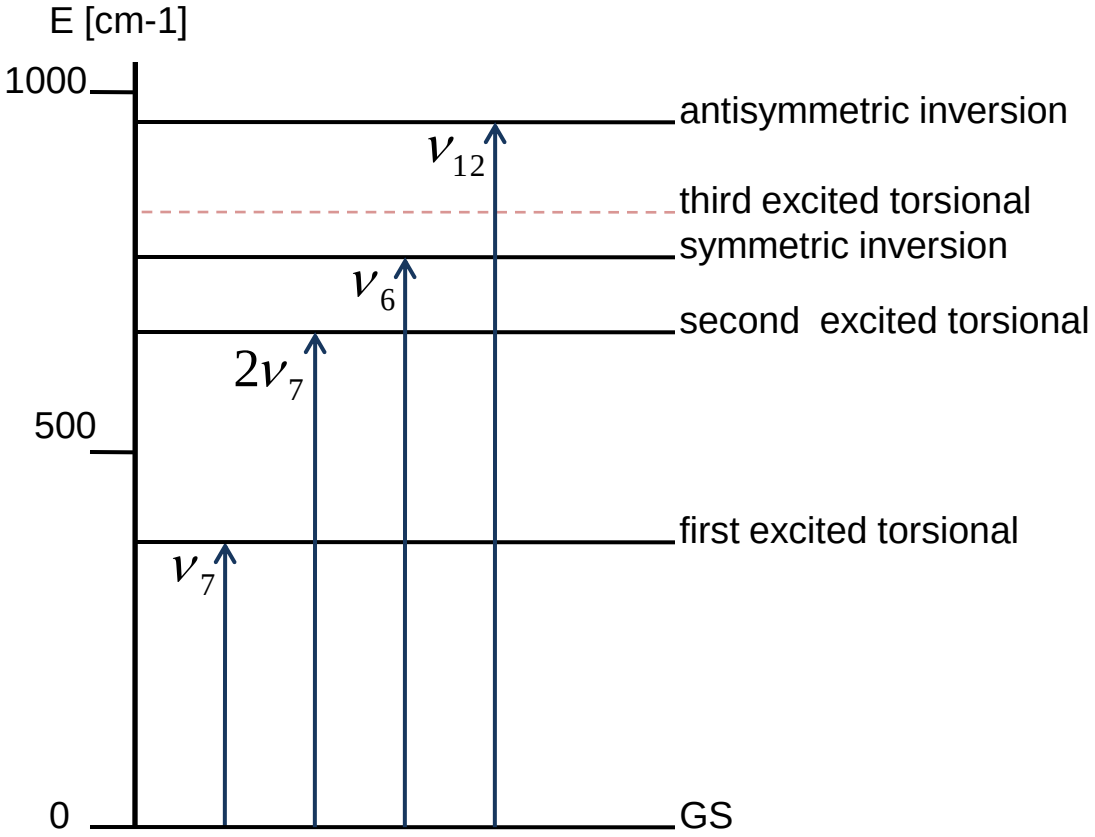
$$\frac{1}{4}\left\langle J, K^{'}, m^{'}, v_1^{'}, v_2^{'} \left| \left(\mu_{\rho_1\rho_1} + \mu_{\rho_2\rho_2}\right)\left(J_{\rho_1}^2 + J_{\rho_2}^2\right) \right| J, K, m, v_1, v_2 \right\rangle =$$

$$= \frac{1}{4}\sum_{i=2}^{6} b_i\left(k, k', l\right)\left\langle J', K'^{\pm} \left\| J, K^{\pm} \right\rangle \right\langle m'^{\pm} \left| \cos l\tau \right| m^{\pm} \right\rangle$$

$$\left\langle \upsilon_1', \upsilon_2'^{\pm} \left| \left(\cos k\rho_1 J_{\rho_1}^2 \cos k'\rho_2 + \cos k\rho_1 \cos k'\rho_2 J_{\rho_2}^2 + \cos k'\rho_1 J_{\rho_1}^2 \cos k\rho_2 + \cos k'\rho_1 \cos k\rho_2 J_{\rho_2}^2 \right) \right| \upsilon_1, \upsilon_2^{\pm} \right\rangle$$

where b_i are coefficients of the Fourier expansion of the term $\left(\mu_{\rho_1\rho_1} + \mu_{\rho_2\rho_2}\right)$.

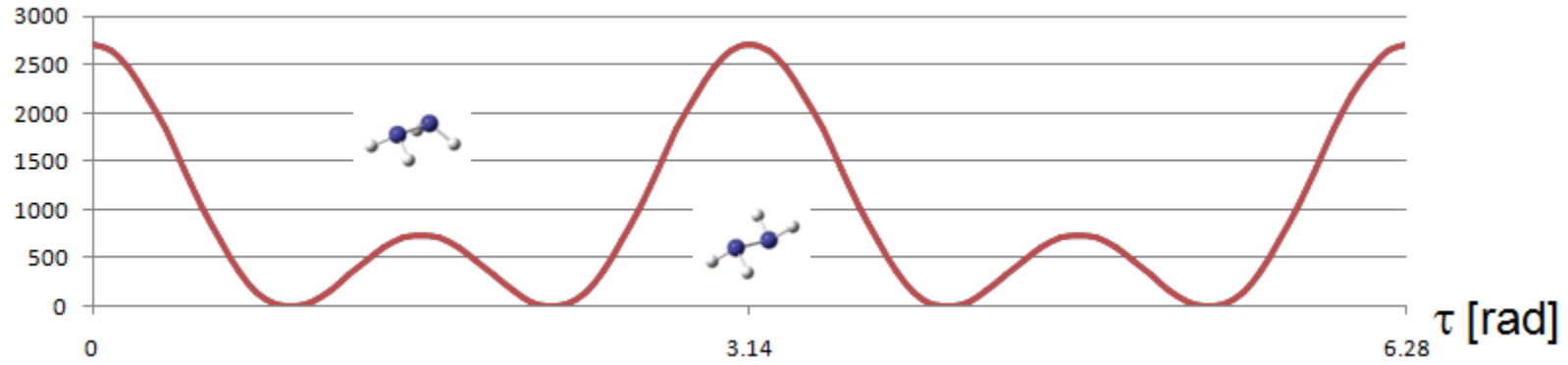
Inversion-torsion energy levels of N_2H_4



Fit to experimental data:

inv-tors level	energy [cm^{-1}]	torsional splitting [cm^{-1}]	inversion splitting [cm^{-1}]
GS	0	0.00019	0.535
ν_7	376.402	0.0608	0.266
$2\nu_7$	670.349	6.6896	0.689
$3\nu_7$	860.138	87.96	0.411
ν_6	795.137	0.510	8.864
ν_{12}	937.156	0.1178	13.735

1-D torsional potential



Torsional potential

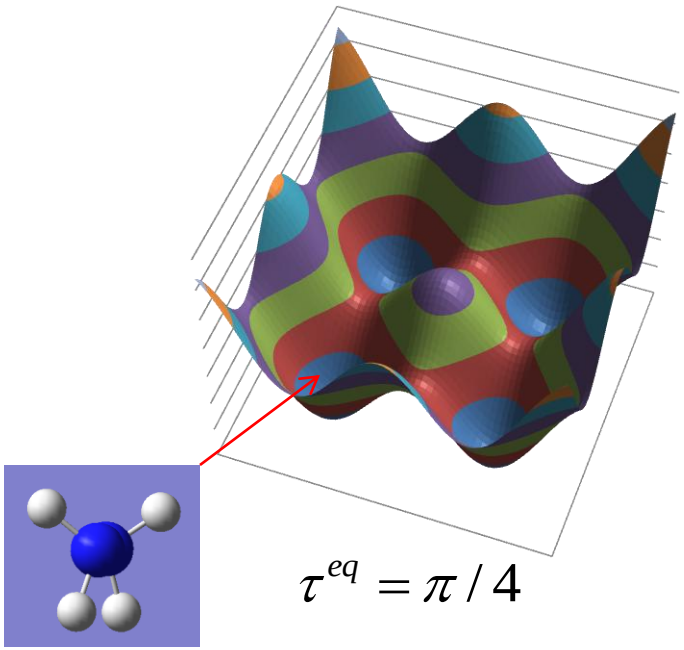
$$V_t(\tau) = V_2 \sin 2\rho_1^{eq} \sin 2\rho_2^{eq} \cos 2\tau + V_4 \cos 4\tau + V_8 \cos 8\tau$$

The fit to experimental data:

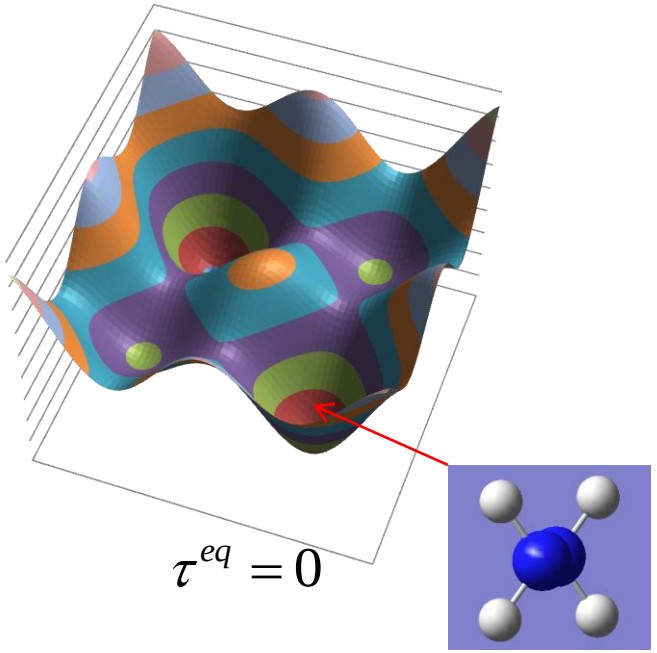
V_2=1008 cm^{-1} V_4=786 cm^{-1} $\rho_1^{eq} = \rho_2^{eq} = 49.8^\circ$

2-D inversion-inversion potential

$$V_i(\rho_1,\rho_2) = a_0 + \sum_{k=1}^{2}\left(a_1\cos\rho_k + a_2\cos 2\rho_k + a_3\cos 3\rho_k + a_4\cos 4\rho_k\right) + V_{22}\cos 2\rho_1\cos 2\rho_2$$
$$+ V_{222}\sin 2\rho_1\sin 2\rho_2\cos 2\tau^{eq}$$



$\tau^{eq} = \pi/4$



$\tau^{eq} = 0$

Potential function parameters

Torsional barrier (trans)	= 744 cm^{-1}
Torsional barrier (cis)	= 2706 cm^{-1}
Inversion barrier (one NH_2 group)	= 1997 cm^{-1}
Inversion barrier (both NH_2 groups)	= 3454 cm^{-1}
Inversion barrier in cis configuration	= 5480 cm^{-1}
Torsional equilibrium angle	= 45.1°
Inversion equilibrium angle	= 54.7°

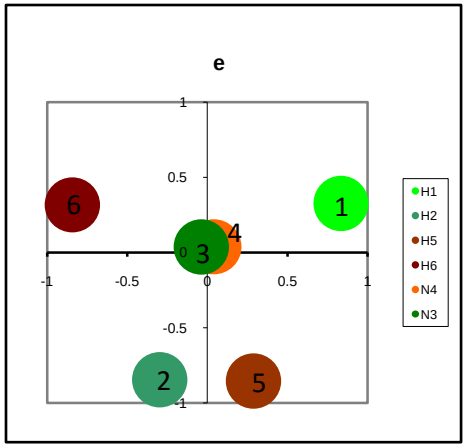
W. Łodyga, J.Makarewicz, „Torsion-wagging tunneling and vibrational states in hydrazine determined from its ab initio potential energy surface”, J.Chem.Phys. **136**, 174301 (2012)

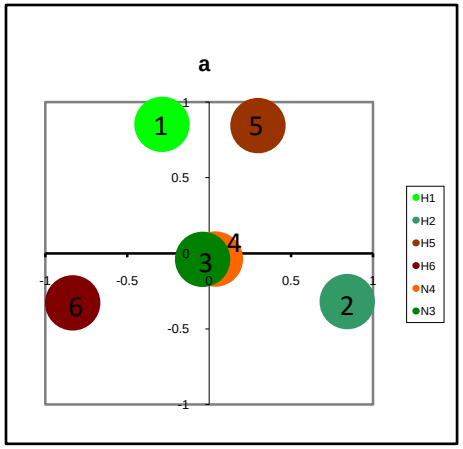
Summary of the direct procedure

1) How to attach the molecular axis system to a molecule?
2) Creation of the PI group of symmetry
3) Transformation of coordinates in the PI group
4) Rotation- vibration basis functions
5) Symmetrized rotation-vibration basis functions
6) Series expansion of the moment of inertia tensor
7) Series expansion of the LAV potential function
8) Hamiltonian matrices in symmetry functions
9) Fit to experimental data – highly non-linear procedure
10) Result: potential function parameters and geometry of the molecule
11) Comment: this procedure must be usually supported by the ab initio calculation

Effective Hamiltonian

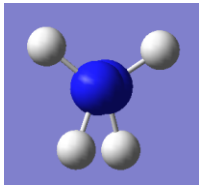
Definition of the localized (slightly distorted) configuration (ρ_1=44°, ρ_2=46°)





Initial configuration

	X	Y	Z
H1	0.8340	0.3270	1.1360
H2	-0.2977	-0.8449	1.1360
N3	-0.0386	0.0373	0.6944
H5	0.2882	-0.8541	-1.1228
H6	-0.8435	0.3178	-1.1228
N4	0.0400	0.0386	-0.6963

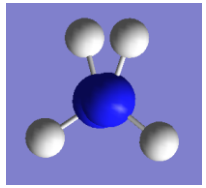


After transformation

(34)(1526)* a

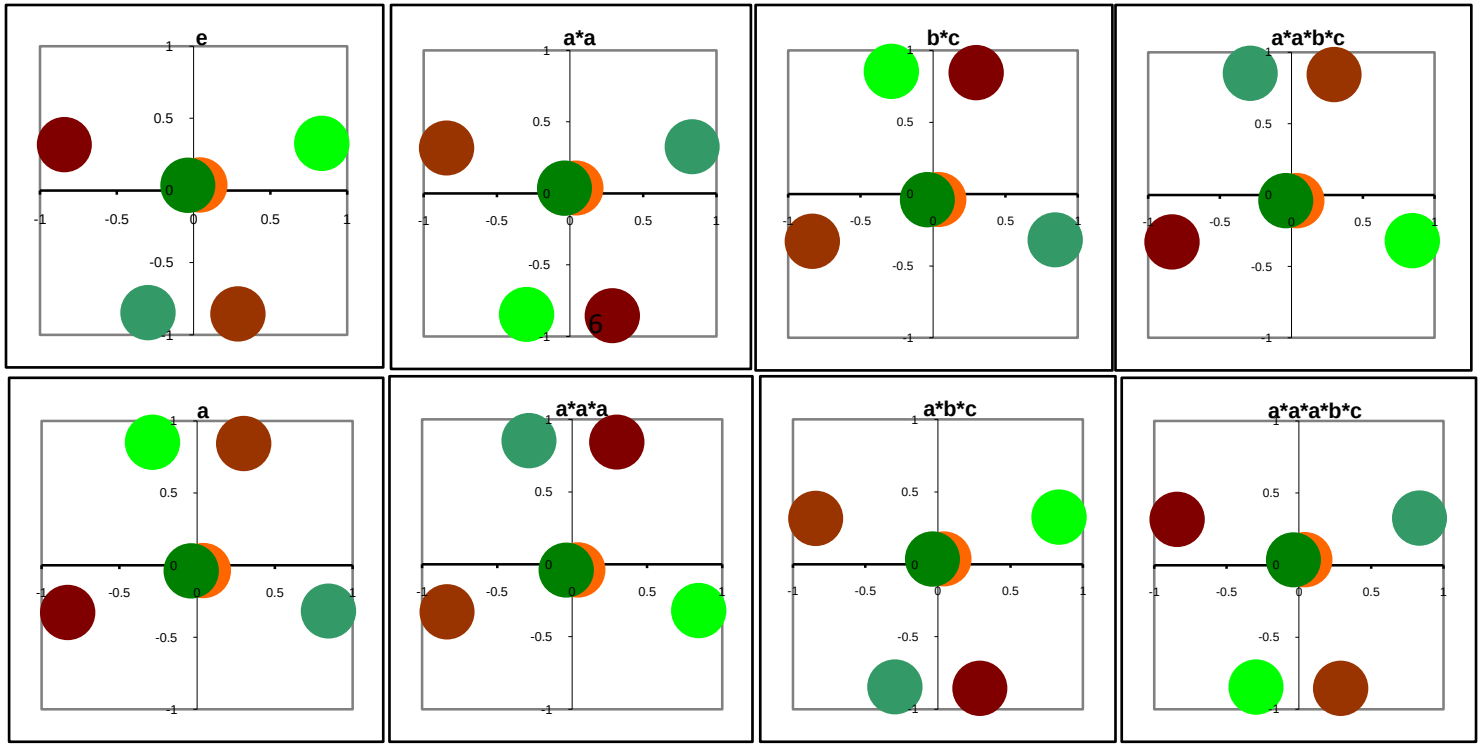
0	0	0	-1	0	0
0	0	0	0	-1	0
0	0	0	0	0	-1
0	-1	0	0	0	0
-1	0	0	0	0	0
0	0	-1	0	0	0

	X	Y	Z
H1	-0.2882	0.8541	1.1228
H2	0.8435	-0.3178	1.1228
N3	-0.0400	-0.0386	0.6963
H5	0.2977	0.8449	-1.1360
H6	-0.8340	-0.3270	-1.1360
N4	0.0386	-0.0373	-0.6944



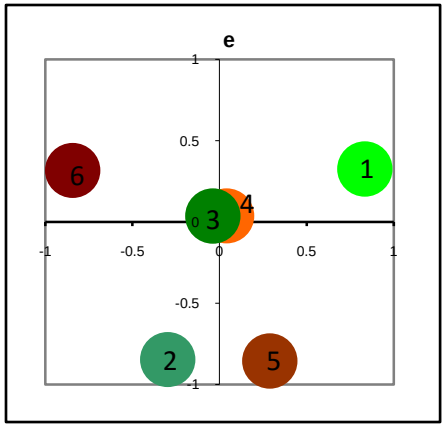
The same effect can be achieved through the coordinate transformation ($\tau \rightarrow -\tau+\pi/2$, $\rho_1 \rightarrow \rho_2$, $\rho_2 \rightarrow -\rho_1$)

8 non-superimposable configurations

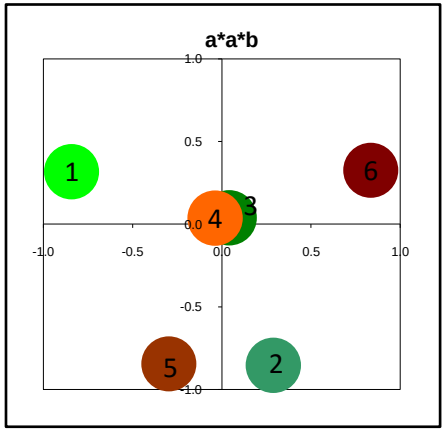


The configurations cannot be superimposed through a rotation in space. The first configuration can be transformed into another one through a proper change of LAV coordinates τ, ρ_1, ρ_2 as defined earlier.

Basis functions



$|1\rangle$



$|1'\rangle$

In every non-superimposable configuration an inversion-torsional function is localized.

$|1'\rangle$ is the $|1\rangle$ function rotated by π, depending on effect of the C_2 rotation it has A or B symmetry type.

The basis functions are built as combinations of both functions $(|1\rangle + |1'\rangle)$ or $(|1\rangle - |1'\rangle)$.
In this method the explicit form of inversion -torsion functions is not important, only their symmetry properties matter.

Symmetrized rot-inv-tors functions

Combinations of inversion-torsion functions localized in 8 non-superimposable configurations belong to symmetry species:

$$A_{1g}^{+}, A_{1u}^{-}, B_{1g}^{+}, B_{1u}^{-}, E^{+}, E^{-}, E_g, E_u, E_1$$

The rotational functions are of $A_{1g}^{+}, A_{2g}^{-}, B_{1g}^{+}, B_{2g}^{-}, E_g$ symmetry.

Thus, the rotation-inversion-torsional functions are of symmetry:

$$A_{1g}^{+}, A_{2g}^{-}, B_{1g}^{+}, B_{2g}^{-}, A_{1u}^{-}, A_{2u}^{+}, B_{1u}^{-}, B_{2u}^{+}, E^{+}, E^{-}$$

Example of a symmetrized function for J=even and K=odd of A_{1g}^{+} symmetry:

$$\left|A_{1g}^{+}(K\geq 0, J)\right\rangle = \frac{1}{\sqrt{2}}\left\{\left|E_g^{(+)}\right\rangle_{tw}\left|J, K^{(-)}\right\rangle + (-1)^{\frac{(K-1)}{2}} i \left|E_g^{(-)}\right\rangle_{tw}\left|J, K^{(+)}\right\rangle\right\}$$

$$\left|E_g^{(+)}\right\rangle = \frac{1}{2}\left[|1\rangle - |2\rangle + |3\rangle - |4\rangle\right] \qquad \left|E_g^{(-)}\right\rangle = \frac{1}{2}\left[|5\rangle - |6\rangle - |7\rangle + |8\rangle\right]$$

Rovibrational effective Hamiltonian

$$H = \sum_{n=1}^{8} H_n = \sum_{n=1}^{8} h_n + h_{nj} J^2 + h_{nk} J_z^2 + h_{njj} J^4 + h_{njk} J^2 J_z^2 + h_{nkk} J_z^4 +$$
$$f_n \left(J_+^2 + J_-^2 \right) + g_n \left[i \left(J_+^2 - J_-^2 \right) \right] + q_n J_z +$$
$$d_n \left(J_+^4 + J_-^4 \right) + p_n \left[i \left(J_+^4 - J_-^4 \right) \right] +$$
$$\left[r_{n+} J_+ + r_{n-} J_- \right] + \left[s_{n+} \left(J_z J_+ + J_+ J_z \right) + s_{n-} \left(J_z J_- + J_- J_z \right) \right]$$

The sum runs over 8 non-superimposable configurations of hydrazine.

The Hamiltonian matrix is built from products of rotational and inversion-torsion function.

Example: $\langle inv.tors | q_n | inv.tors \rangle \langle rot | \hat{J}_z | rot \rangle$

Matrix elements – transformations under PI operations of $G_{16}^{(2)}$

How to simplify a matrix element?

$$\langle inv.tors|q|inv.tors\rangle \qquad q \in A_{2g}^{-} \qquad \hat{J}_z \in A_{2g}^{-}$$

$$\langle inv.tors|q|inv.tors\rangle = \tfrac{1}{4}\{[\langle 1| - \langle 2| + \langle 3| - \langle 4|]q[|5\rangle - |6\rangle - |7\rangle + |8\rangle]\}$$

An inv.tors component is built from a sum of integrals describing interactions between different configurations.
The symmetry properties of the configurations are used to reduce the integrals to a form $\langle 1|q|n\rangle$

Example: $b\langle 2|q|5\rangle = \langle 1|(-q)|5\rangle = -\langle 1|q|5\rangle$

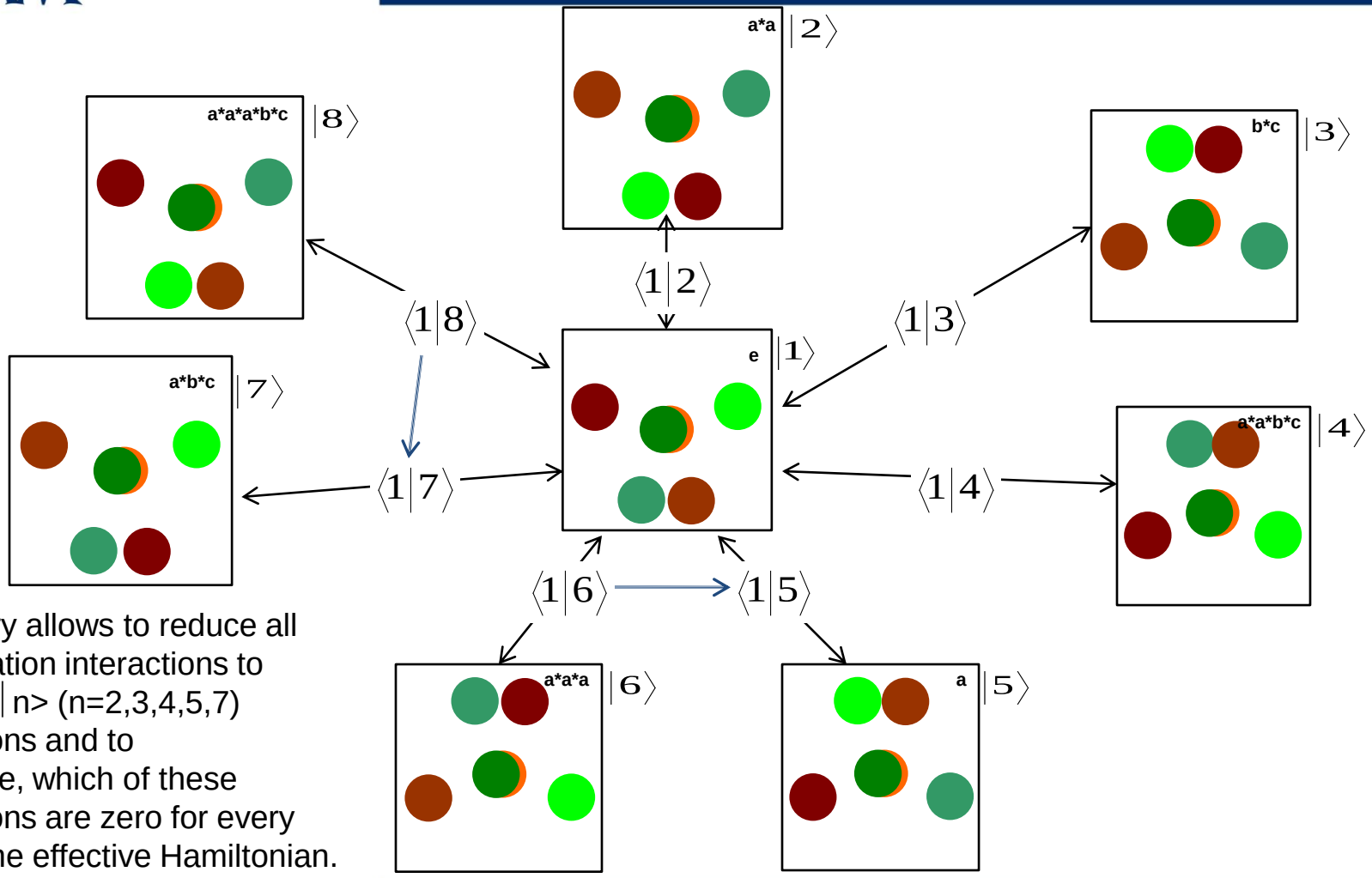
$$\langle inv.tors|q|inv.tors\rangle = \langle 1|q|5\rangle - \langle 1|q|6\rangle - \langle 1|q|7\rangle + \langle 1|q|8\rangle$$

The symmetry properties can be further used to remove some of $\langle 1|q|n\rangle$ integrals

$a^2b\langle 1|q|6\rangle = \langle 1|(-q)|5\rangle = -\langle 1|q|5\rangle$ $\qquad$ $a^2b\langle 1|q|8\rangle = \langle 1|(-q)|7\rangle = -\langle 1|q|7\rangle$

Finally: $\boxed{\langle inv.tors|q|inv.tors\rangle = 2\langle 1|q|5\rangle - 2\langle 1|q|7\rangle}$

Configuration interactions

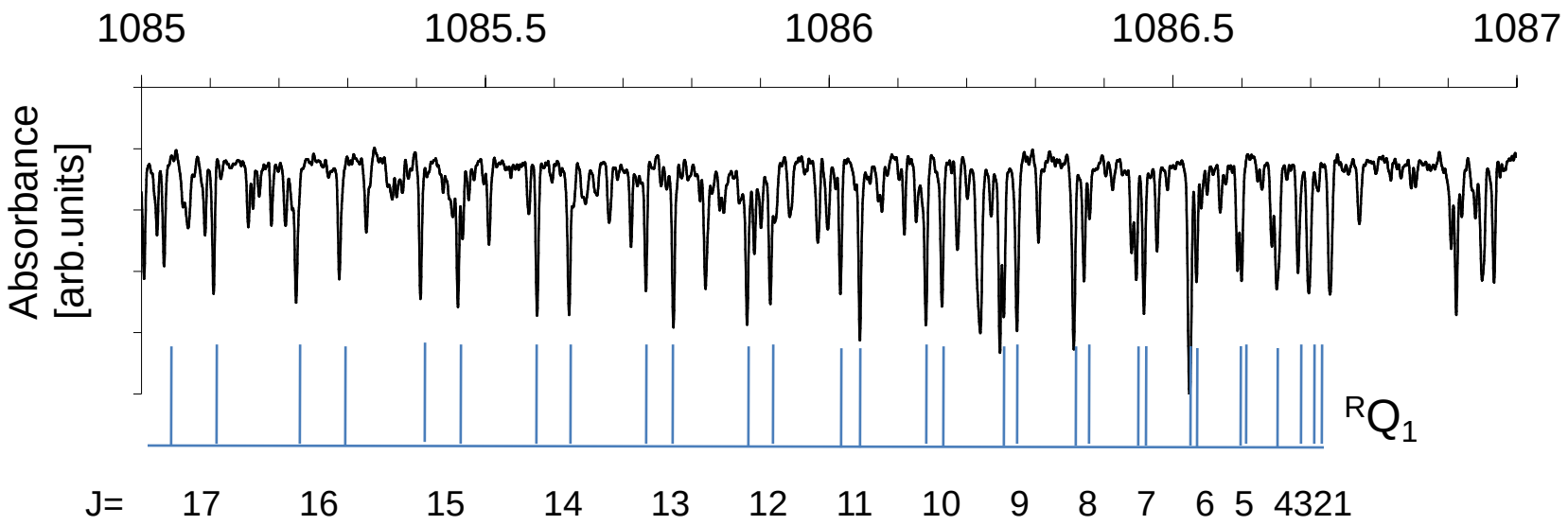


Symmetry allows to reduce all configuration interactions to basic <1|n> (n=2,3,4,5,7) interactions and to determine, which of these interactions are zero for every term in the effective Hamiltonian.

Summary of the effective Hamiltonian procedure

1) How to attach the molecular axis system to a molecule?
2) Creation of the PI group of symmetry
3) Non-superimposable configurations of the molecule
4) Transformation of configurations in the PI group (double-group)
5) Effective localized inversion-torsion basis functions
6) Symmetrized inversion-torsion basis functions
7) Hamiltonian matrices in symmetrized functions
8) Determination of non-zero matrix elements from the analysis of their symmetry properties in the $G_{16}^{(2)}$ group and under the time reversal operation
9) Fit to experimental data – almost linear procedure
10) Result: rotational parameters and tunneling splittings

NN stretching band ν_5 for hydrazine



In the Q branch the observed doublets originate from lower levels of A_{1U}^{-}, A_{2U}^{+} symmetry.

1500 transitions with a resolution of 0.002 cm^{-1} for K' from 0 to 6 and for all symmetry species have been analyzed.

I.Gulaczyk, M.Kręglewski, A.Valentin, *J.Mol.Spectrosc*. **220**, 132-136 (2003)

Effective parameters for IR bands of hydrazine

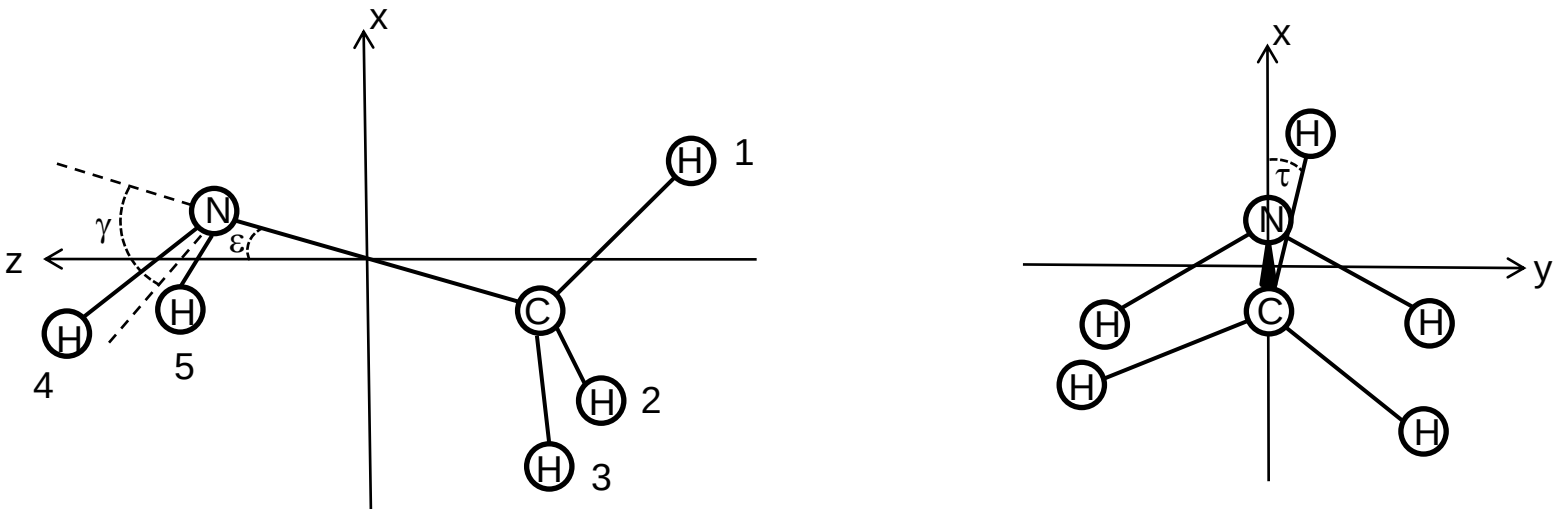
		G.S.	ν_7 torsional	$2\nu_7$ second torsional	ν_{12} inv.antisym.	ν_6 inv.sym.	$3\nu_7$ third torsional	ν_5 N-N stretching
energy	**cm^{-1}**	**0.0**	**376.40215(13)**	**670.34902(12)**	**937.1437(25)**	**795.057(38)**	**860.057(38)**	**1077.24164(10)**
A	MHz	143459.1491(250)	142212.06(20)	141139.91(36)	144655.2(28)	143925.(17)	139486.(17)	143438.72(51)
(B+C)/2	MHz	24075.81466(450)	23944.967(50)	23802.826(65)	24077.01(39)	23960.6(34)	23643.8(29)	23901.64(23)
B-C	MHz	12.90030(200)	184.52(30)	537.46(45)	-0.32(35)	207.1(63)	600.	14.73(50)
DJ	kHz	56.80610(810)	58.66(19)	62.80(25)	57.99(40)	59.6(87)	58.	53.70(52)
DJK	kHz	389.232(130)	366.4(11)	427.7(36)	545.16(44)	354(51)	366.	312.9(68)
DK	kHz	2007.651(660)	1799.9(34)	1985.5(74)	2283(19)	3097(200)	1800.	2797(76)
h2v	MHz	-4.7470(150)	-0.73(80)	-110.3(19)	-1434(49)	1868(110)	-0.73.	-1316(16)
h3v	MHz	-2.8373(160)	-912.0(21)	-100274.6(30)	?	-6740(930)	-1319341.(3100)	?
h5v	MHz	-4010.1198(200)	1994.1(16)	-5165.2(19)	102775(51)	-68826(190)	3000.	-36019(15)
q5	MHz	-14.3403(110)	-5.49(30)	-0.543(91)	46.1(97)	564(61)	-500.	-969.5(50)
g5	MHz	-0.143810(130)	-0.068(11)	-1.29(12)	0.23(30)	-19.64(93)	-.07	-3.63(17)
						Fermi resonance		
						w_1 /MHz	-597187.(1600)	
						w_{1K} /MHz	278(15)	
						w_5 /MHz	-2635(220)	
				# lines	3682	1096	120	1454
				# param.	19	24		20
				highest K'	13	9	3-9	6
				std.dev. cm^{-1}	0.061	0.108	0.091	0.011

torsional splitting $\approx 2\ h_{3v}$

inversion splitting $\approx 4\ h_{5v}$

Is the rovibrational problem for methylamine very different from that for hydrazine?

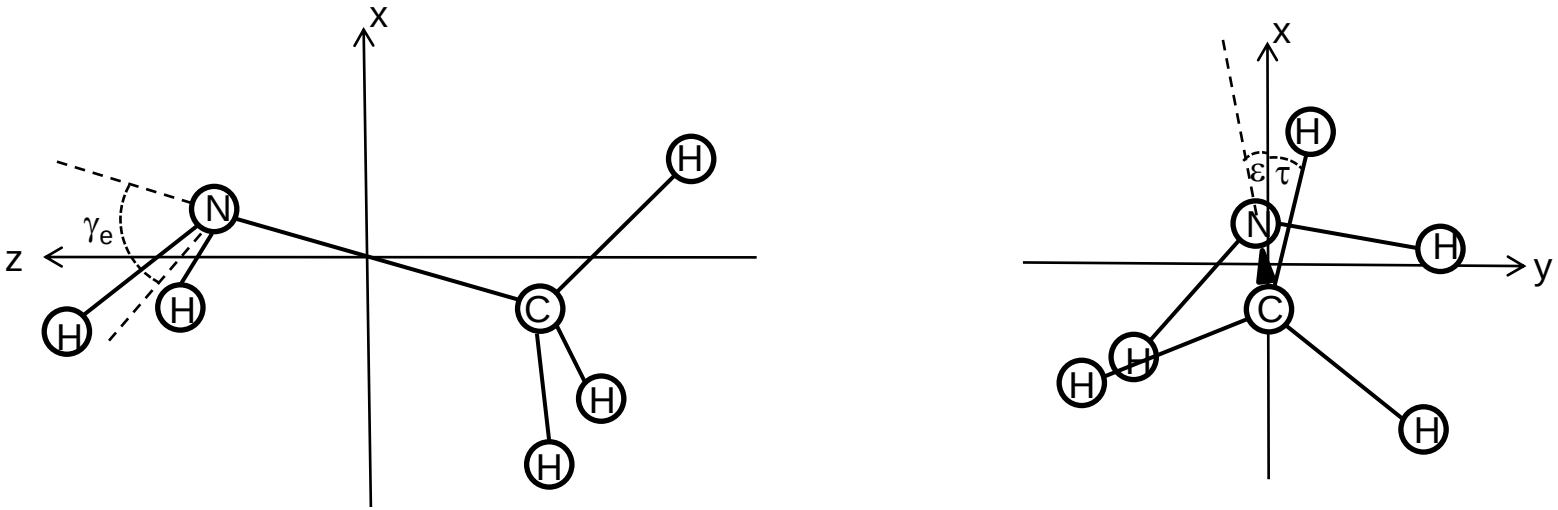
Explicit rovibrational Hamiltonian of CH_3NH_2



The angle ε changes with the inversion angle γ to minimize the inversion-rotation coupling.

The NH_2 group is fixed in the molecular axis system, which leads to a strong coupling between torsion and rotation.

Effective Hamiltonian of CH_3NH_2



The angle ε changes with the torsional angle τ to minimize the inversion-rotation coupling.

$$\varepsilon = -\rho\tau$$ where $$\rho = \frac{I_{CH_3}}{I_{CH_3NH_2}} = \frac{p}{m}$$ p,m are integer numbers

PI group of CH_3NH_2

Permutation-inversion generators of G_{12} group
a=(123)(45)
b=(23)(45)*

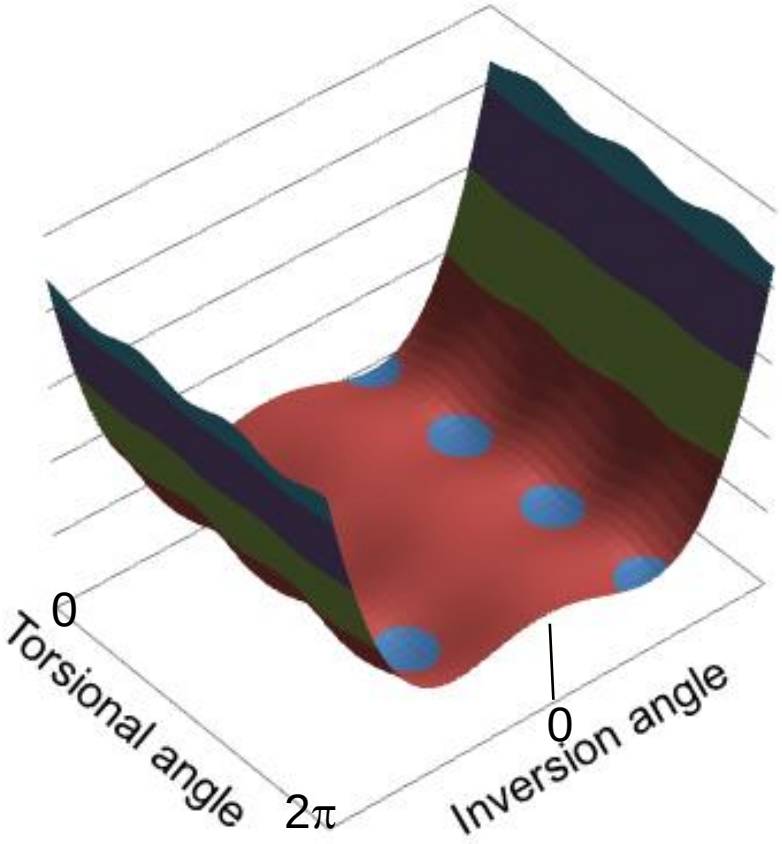
Explicit Hamiltonian

E	***a***	***b***
χ	$\pi+\chi$	χ
θ	θ	$\pi-\theta$
φ	φ	$\pi+\varphi$
τ	$\tau-\pi/3$	$-\tau$
γ	$-\gamma$	γ

Effective Hamiltonian

E	***a***	***b***
χ	$\pi+\chi-2\pi p/(6m)$	$\pi-\chi$
θ	θ	$\pi-\theta$
φ	φ	$\pi+\varphi$
τ	$\tau-2\pi/3$	$-\tau$
γ	$-\gamma$	γ

Potential for expilcit Hamiltonian



Rotation-inversion-torsion Hamiltonian

$$\hat{H}_{itr} = \hat{H}_i + \hat{H}_t + \hat{H}_r$$

$$\hat{H}_i = \tfrac{1}{2}\mu_{\gamma\gamma} J_\gamma^2 + V_i(\gamma)$$

$$\hat{H}_t = \tfrac{1}{2}\mu_{\tau\tau} J_\tau^2 + V_t(\gamma,\tau)$$

$$\hat{H}_r^{(1)} = \tfrac{1}{2}\mu_{zz} J_z^2 + \tfrac{1}{2}\mu_{z\tau} J_z J_\tau$$

$$\hat{H}_r^{(2)} = \tfrac{1}{4}(\mu_{xx} - \mu_{yy})(J_x^2 - J_y^2) + \tfrac{1}{4}(\mu_{xx} + \mu_{yy})(J_x^2 + J_y^2) + \tfrac{1}{2}\mu_{xz}(J_x J_z - J_z J_x) + \tfrac{1}{2}\mu_{x\tau} J_x J_\tau$$

Solution:

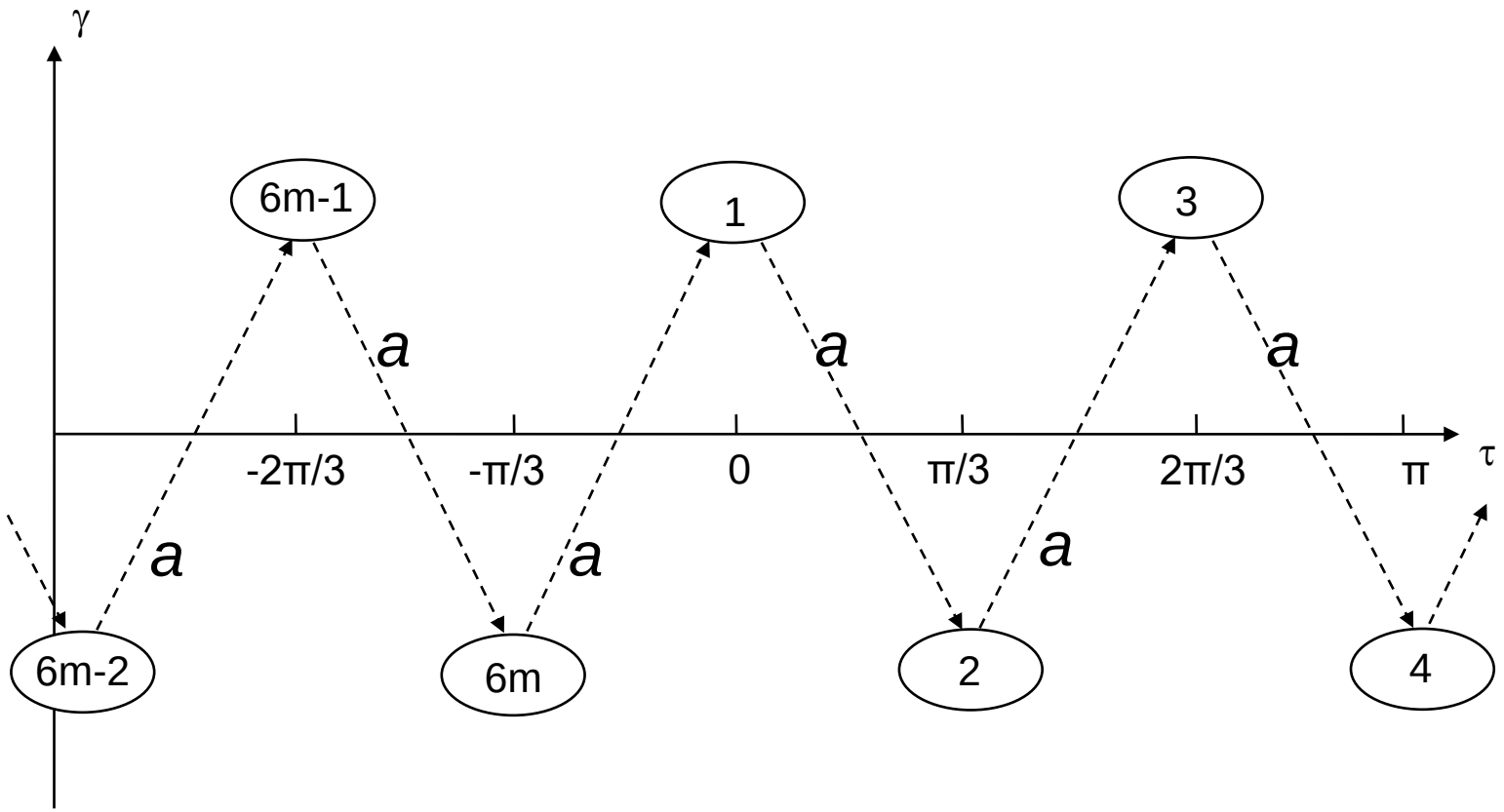
1) Numerical solution of the inversion problem $|v\rangle$

2) Solution of the inversion-torsion-K rotation $|k\rangle \sum_{v,m} c_{rk}(v,m)|v\rangle|m\rangle$

3) Final solution $\sum_{k=0}^{J} \sum_{r} a(k,r)|k\rangle \sum_{v,m} c_{rk}(v,m)|v\rangle|m\rangle$

Notice: all basis functions are symmetrized

Potential for effective Hamiltonian



Effective Hamiltonian for CH_3NH_2

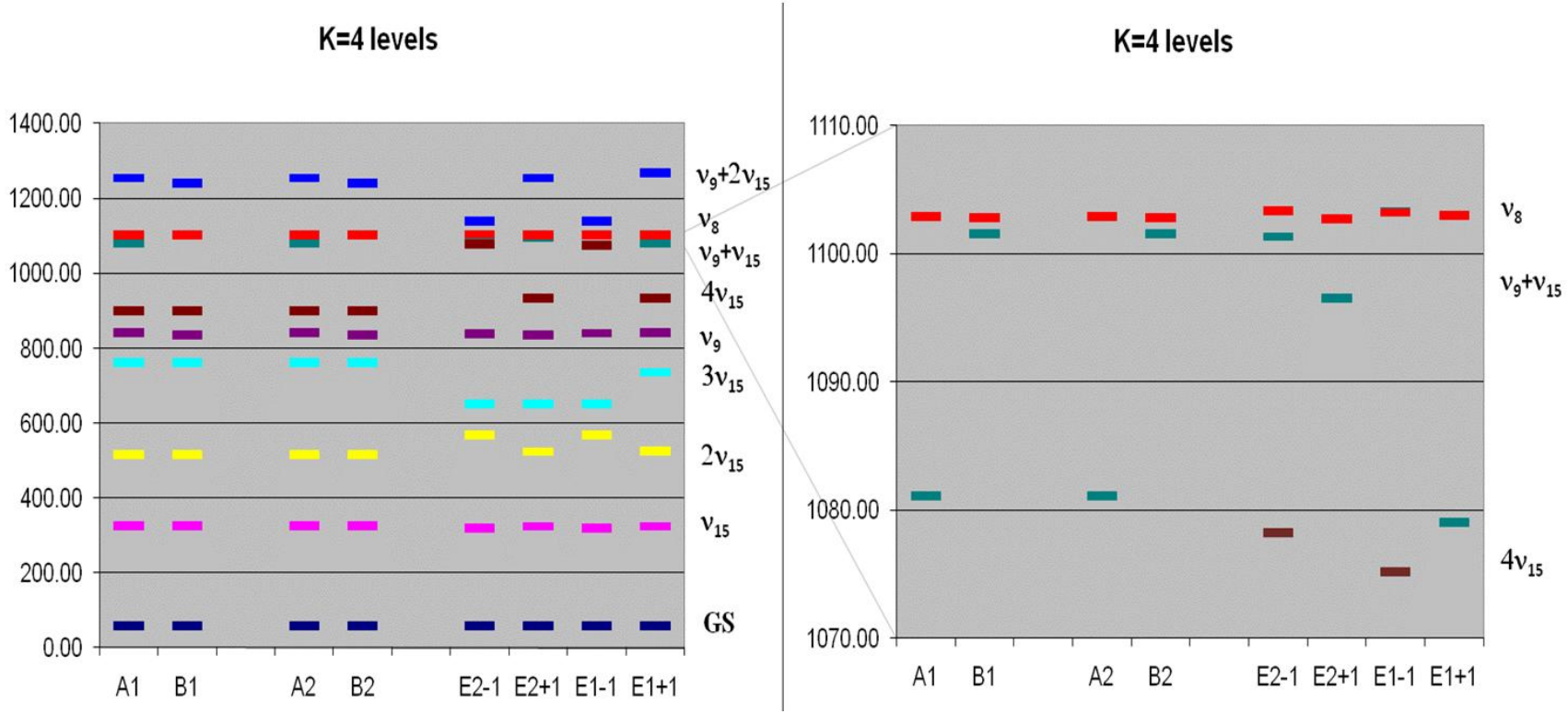
$$H=\sum_{n=1}^{3m}H_n=\sum_{n=1}^{3m}\left\{\begin{array}{l} h_n+h_{nj}J^2+h_{nk}J_z^2+h_{njj}J^4+h_{njk}J^2J_z^2+h_{nkk}J_z^4+ \\ f_n\left(J_+^2+J_-^2\right)+g_n\left[i\left(J_+^2-J_-^2\right)\right]+d_n\left(J_+^4+J_-^4\right)+p_n\left[i\left(J_+^4-J_-^4\right)\right]+ \\ \left[r_{n+}J_++r_{n-}J_-\right]+\left[s_{n+}\left(J_zJ_++J_+J_z\right)+s_{n-}\left(J_zJ_-+J_-J_z\right)\right] \end{array}\right\}2\cos\left[(n-1)\rho\tau\right]+$$

$$+\sum_{n=2}^{3m}2iq_nJ_z\sin\left[(n-1)\rho\tau\right]$$

n is the ordinal number of a molecular configuration interacting with the configuration number 1

Contrary to the effective Hamiltonian for hydrazine (8 configurations)in methylamine the lenght of the expansion is not determined (3m configurations)

Combination of explicit and effective Hamiltonians



Calculated with the explicit method torsional and inversion states of CH3NH2 were used to analyze the observed perturbations in the $\nu 8$ C-N stretching band

Thank you!

Let me mention two scientists from whom I have learned a lot about hydrazine and methylamine:

Jon T. Hougen

Nobukimi Ohashi

and my colleagues from Poznań

Iwona Gulaczyk

Wiesław Łodyga

Jan Makarewicz